

Comparative study between two quantum spin systems KCuCl₃ and TlCuCl₃

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Abstract. – We have performed an *ab initio* study of the electronic structure of two isostructural quantum spin systems, KCuCl₃ and TlCuCl₃, which have recently attracted much attention due to their unconventional magnetic properties. Our first-principles analysis shows unambiguously the role of Tl, as opposed to structural differences between the two compounds, in making TlCuCl₃ a *strongly* coupled $s=\frac{1}{2}$ dimer system compared to KCuCl₃ which shows a *weakly* coupled $s=\frac{1}{2}$ dimer behavior. Good agreement with the existing analysis of inelastic neutron scattering results has been observed.

Introduction.– The behavior of low-dimensional quantum spin systems is dominated by zero-point spin fluctuations. As a consequence, they show a variety of interesting magnetic properties which are not present in their classical counterparts. In the last years a great amount of effort, both theoretically and experimentally, has been dedicated to the study of these quantum spin systems. An important example of such systems are materials having a singlet ground state with a finite energy gap in the spin excitation spectra like even-leg ladder compounds [1], $s=\frac{1}{2}$ alternating chain compounds [2], spin-Peierls [3] or spin-dimer compounds [4]. In particular, the family of coupled spin-dimer systems ACuCl₃ ($A = K, Tl$) is being currently intensively studied in connection to its magnetic properties. KCuCl₃ has a spin excitation gap $\Delta \sim 2.6$ meV and the analysis of inelastic neutron scattering (INS) [5,6] data indicate that this system is a spin-dimer system with *weak* three-dimensional interdimer couplings. TlCuCl₃, though being isostructural to KCuCl₃, has a spin excitation gap $\Delta \sim 0.65$ meV about four times smaller than that of KCuCl₃ and a saturation field twice as large as that for KCuCl₃. Accordingly, the behavior of this system has been proposed [7,8] to be that of a three-dimensional *strongly* coupled spin-dimer system. The small size of the spin gap makes these compounds very suitable for studying the effects of the application of an external magnetic field on the quantum properties of the system. Recently [9], magnetic field-induced Néel ordering has been observed in TlCuCl₃ for magnetic fields H higher than the gap field $H_g = \Delta/g\mu_B \sim 6$ T and has been interpreted as a Bose-Einstein condensation of excited triplets

(magnons) [10]. New nuclear magnetic resonance (NMR) investigations [11] have also shown that this phase transition is accompanied by changes in the crystal lattice parameters, what is an indication of an important spin-phonon coupling in this material. The observation of field-induced phase transition has been also reported in KCuCl_3 for a magnetic field $H > H_g \sim 22$ T [12]. Magnetization measurements [13] were also performed in the mixed spin system $(\text{Tl}_{1-x}\text{K}_x)\text{CuCl}_3$ where the x substitution creates bond randomness in the system and the field-induced phase transition was studied as a function of the K concentration. Motivated by the great amount of exotic phenomena observed in these materials, we have carried out first principles study of the electronic properties of these systems in order to give a microscopic foundation to their behavior and analyze the similarities and differences between the two systems.

Crystal Structure.- Both KCuCl_3 and TlCuCl_3 crystallize in the monoclinic $P2_1/c$ space group [14] with four formula units per unit cell. The lattice parameters for KCuCl_3 are given by $a = 4.029\text{\AA}$, $b = 13.785\text{\AA}$, $c = 8.736\text{\AA}$ and $\beta = 97.20^\circ$, while those for TlCuCl_3 are $a = 3.982\text{\AA}$, $b = 14.144\text{\AA}$, $c = 8.890\text{\AA}$ and $\beta = 96.32^\circ$. Therefore, compared to KCuCl_3 , the TlCuCl_3 lattice is somewhat compressed along the a -axis and enlarged in the bc plane. The degree of monoclinicity also varies by some extent. Both structures are formed by edge-sharing CuCl_6 octahedra which build zig-zag chains running along the a -axis (fig. 1). These chains are located at the corners and center of the unit cell in the bc plane. K^+/Tl^+ ions are distributed in between these chains. The CuCl_6 octahedra are highly distorted due to the Jahn-Teller active Cu^{2+} ion with large elongation along one direction resulting into nearly planar Cu_2Cl_6 dimer clusters which are the basic unities in the structure (marked with the box in fig. 1).

Band Structure.- In panels (a) and (b) of fig. 2 we show the band-structures of KCuCl_3 and TlCuCl_3 along various symmetry directions. First-principles Density Functional Theory (DFT) calculations have been carried out within the framework of the state-of-art full-potential linearized augmented plane wave (LAPW) method [15] and the linearized muffin tin orbital (LMTO) method [16] based on the local-density-approximation (LDA). The band-structures obtained by the two methods are in overall agreement with each other. The predominant features of the band structure are the complex of four narrow bands close to the Fermi level formed by Cu $d_{x^2-y^2}$ orbitals (in the local frame of reference) contributed by each Cu atom in the unit cell, admixed with Cl p-states. These bands are half-filled and the insulating groundstate observed in these compounds should be explained by the effect of strong correlations which are not fully considered in the LDA approximation. This set of bands is separated from the low-lying valence bands by a gap of about 0.3 to 0.5 eV [17] and from the high-lying excited bands, which are dominated by states from the K/Tl atoms, by another gap of about 3 eV. Concentrating on the low-energy bands close to the Fermi-level, we see that the bands are dispersive along all the symmetry directions suggesting the compounds to be three-dimensionally coupled systems in agreement with the findings of INS measurements [5, 6, 7, 8]. Since the dispersion behavior is similar between KCuCl_3 and TlCuCl_3 , the predominant interaction pathways should be alike for both compounds. The total bandwidth of the four-band complex close to the Fermi level is somewhat larger for TlCuCl_3 (≈ 0.5 eV) compared to that of KCuCl_3 (≈ 0.4 eV) suggesting the intradimer coupling to be stronger in TlCuCl_3 than in KCuCl_3 . We also observe here that the bands in TlCuCl_3 are in general more dispersive than in KCuCl_3 what indicates larger interdimer interactions in TlCuCl_3 compared to KCuCl_3 [18].

This change in the strength of the intra- and interdimer couplings between the two compounds could be caused by (i) the changes in the structural parameters between the two compounds or by (ii) the role of the Tl^+ ion compared to that of the K^+ ion. In order to

have an understanding of which of these effects determines predominantly the behavior of these systems, we have carried out model calculations of KCuCl_3 by considering the structural parameters of the Tl-compound and viceversa, we computed TlCuCl_3 by considering the structural parameters of the K-compound. The corresponding band structures are shown in panels (c) and (d) of fig. 2. As we see, changing the lattice parameters has a minor effect on the band structure (compare fig. 2(a) and fig. 2(c)) while substituting K^+ by Tl^+ in the same lattice has a significant effect making the band dispersions comparable to that of the Tl-compound. This exercise already points unambiguously to the role of the Tl^+ ion in enhancing the strength of the coupling as compared to that of changes in the structural parameters. In the next section we will make this analysis more quantitative in terms of various hopping integrals.

Low-energy Hamiltonians: Hopping integrals.- We have used the LMTO-based downfolding method, which has been proposed, implemented [19] and applied to a number of cases [20] in recent years, in order to obtain the low-energy effective Hamiltonians that describe the behavior of a system. This method of deriving the low-energy Hamiltonians by integrating out (downfolding) the high energy degrees of freedom results in Hamiltonians defined in the basis of effective orbitals. The process takes into account the proper effective contribution from the orbitals that are being downfolded. For the present compounds, we have derived the low-energy Hamiltonians defined in the basis of effective Cu $d_{x^2-y^2}$ orbitals, by keeping only the $d_{x^2-y^2}$ orbital for each Cu atom in the unit cell and integrating out all the rest. The Fourier transform of this few-orbital downfolded Hamiltonian provides the various hopping integrals, t_{ij} , between these effective orbitals and the corresponding tight-binding (TB) Hamiltonian can be written as $H = \sum_{(i,j)} t_{ij}(c_i^\dagger c_j + h.c.)$ where i and j denote a pair of Cu^{2+} ions. These hopping integrals thus, form the first-principles set of parameters obtained without any fitting procedure containing the fingerprint of the pathways involved in the hopping processes.

Table I shows the various hopping integrals for KCuCl_3 , TlCuCl_3 and the two model compounds KCuCl_3 considering the lattice parameters of TlCuCl_3 and TlCuCl_3 in the lattice of KCuCl_3 . The various hopping pathways are marked in fig. 1. The hoppings are named according to the various magnetic couplings shown in fig. 1 of ref. [8] i.e. $t(l\ m\ n)$ ($t'(l\ m\ n)$) denote the hopping parameters between two equivalent (nonequivalent) sites (in terms of the corresponding spins for magnetic interaction) in dimers separated by a lattice vector $\vec{r} = la\hat{x} + mb\hat{y} + nc\hat{z}$. In Table I we also show the magnetic couplings obtained in various references by fitting the experimental INS data.

Although, due to the complexity of the exchange pathways, there are no simple relationships connecting the hopping and magnetic exchange integrals, the relative strength of the hopping parameters in the K- and Tl-compound can be easily noticed to be in good qualitative agreement with the relative strength shown by the magnetic exchange parameters.

Considering first the intradimer coupling, the distortion in the nearest neighbor Cu-Cl-Cu dimer bond (see the marked box in fig. 1) from 90° towards a linear bonding of 180° angle increases the importance of the antiferromagnetic (AF) coupling over the ferromagnetic (FM) coupling. The Cu-Cl-Cu bond angles in these compounds are $\approx 96^\circ$ which is larger than 94° , the *upper bound* angle given in the edge-shared cuprates [21] for a possible ferromagnetic coupling, thereby providing the intradimer exchange coupling J of AF nature. Considering the superexchange mechanism to be the effective mechanism of exchange in the dimer, and therefore relating the magnetic exchange integral J with the hopping integral t through $J=4t^2/U$ where U is the effective on-site Coulomb repulsion, we observe that the ratio $t_{\text{KCuCl}_3}^2/t_{\text{TlCuCl}_3}^2 \sim 0.75$ obtained from the *ab initio* analysis compares very well with the ratio of J 's obtained by fitting the INS data, 0.76 in ref. [8] and 0.79 in ref. [7].

Focusing now on the interdimer interactions, note that the values of the hopping matrix elements in TlCuCl_3 are larger than those for KCuCl_3 , thus concluding that TlCuCl_3 will be a strongly coupled dimer system compared to KCuCl_3 which can be characterized as a weakly coupled dimer system in agreement with the conclusions drawn from INS data and already conjectured from band dispersions. Quantitatively, the largest enhancement of the interdimer coupling between TlCuCl_3 and KCuCl_3 occurs for neighboring dimers in the $(1,0,-2)$ plane, i.e. $(l\ m\ n) = (2\ 0\ 1)$. The other dominant interdimer hoppings are $t(1\ 1/2\ 1/2)$ and $t(1\ -1/2\ 1/2)$ [22], the last one being significantly enhanced in the TlCuCl_3 system compared to that of KCuCl_3 . The LDA band dispersions of the four-band complex are reproduced reasonably well by considering the intradimer hopping matrix element and the following interdimer hoppings $t(2\ 0\ 1)$ and $t(1\ 1/2\ 1/2)$ for KCuCl_3 and the additional hopping of $t(1\ -1/2\ 1/2)$ for TlCuCl_3 .

The analysis of the two model calculations (panel (c) and (d) of fig. 2) shows the evident role of the Tl^+ ion in enhancing the hopping matrix elements between the Cu^{2+} ions. Comparing the 2nd and 5th column of Table I, the hopping matrix elements turn out to be similar between KCuCl_3 and the model system KCuCl_3 in the lattice of TlCuCl_3 , while keeping the lattice parameters fixed and substituting K by Tl, the hoppings are affected significantly (4th column) with larger intra- and interdimer hoppings ⁽¹⁾. In order to quantify the action of Tl^+ , we show in fig. 3 the Tl and K partial density of states (PDOS) in TlCuCl_3 and KCuCl_3 respectively. As one sees, the contribution of Tl in the four narrow low energy bands is much larger compared to that of K which implies larger hybridization of Tl with the Cu $d_{x^2-y^2}$ orbitals in TlCuCl_3 compared to that of K in KCuCl_3 . This relatively large hybridization effect from the Tl atoms situated in between the double chains can be understood in terms of the proximity of the Cu $d_{x^2-y^2}$ and the Tl $6s, 6p$ energy states as well as the extended nature of these orbitals in comparison to K $4s$. This behavior leads to a strongly coupled network of Cu-dimers in TlCuCl_3 , while KCuCl_3 behaves as a collection of Cu-dimers weakly interacting in three-dimensions. This description is also supported by electron density analysis of the LDA results. Interestingly, this conclusion is opposite to the case of CaV_2O_5 and MgV_2O_5 where the subtlety in structural differences turn out to be responsible for the differences in the behavior of the two systems [23].

Conclusions.- We have presented a comparative *ab initio* study of the electronic properties of KCuCl_3 and TlCuCl_3 , two isostructural quantum spin systems which have been the subject of recent interest due to their unconventional magnetic properties. It has been the purpose of this study: (i) to obtain a microscopic description of the properties of these systems and its comparison with the behavior predicted from INS. (ii) to understand the microscopic origin of the different behavior between these two compounds.

By means of the downfolding-TB analysis which reduces the information provided by LDA to an effective low-energy Hamiltonian in tight-binding basis, we could successfully corroborate the coupled dimer behavior predicted for these systems by INS. In agreement with the predictions from the INS data analysis, we found in KCuCl_3 the interdimer couplings to be weak, while TlCuCl_3 manifests itself as a strongly coupled dimer system. We also showed that the origin of the differences in the interdimer coupling between the two systems is related to the relative contribution of Tl compared to that of K to the chemical bonding between two

⁽¹⁾Considering the model calculation of TlCuCl_3 in the lattice of KCuCl_3 , the lattice shrinks along the b -axis and expands along the a -axis (by a factor 8 smaller than the shrinkage along the b -axis) which is a distortion similar to the recently observed changes in the crystal lattice when the system undergoes a phase transition to a Néel state induced by the application of an external magnetic field [11]. Although the relative change in the b -parameter for this model calculation is much larger than that reported for the field-induced transition, this study may provide indications of the changes in the couplings caused by this strain effect.

Cu^{2+} ions. Our study is also indicative of possible changes that may occur in the coupling constants due to lattice changes caused by strain effects [11].

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- [18] This interpretation can be understood by the fact that the bandstructure of an isolated dimer system (*i.e.* systems having only non-zero intradimer interaction) is formed by two dispersionless bands, the separation of which is proportional to the strength of the intradimer interaction. Switching on the interactions between isolated dimers (inter-dimer interactions) brings in dispersion to the otherwise dispersionless band structure. Therefore, the bandwidth of the four-band complex in the present case gives us an estimate of the intradimer coupling-strength while the degree of dispersion of these bands can be related to the interdimer couplings.
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FIGURE CAPTIONS

1. Structure of KCuCl_3 (TlCuCl_3). Small black and white atoms represent Cu and Cl respectively while the large gray atoms represent K(Tl). The middle double chain is shifted with respect to other two double chains along b -direction by half a lattice constant. Various hoppings are marked (see text for details).
2. Band structure of KCuCl_3 (panel (a)), TlCuCl_3 (panel (b)), KCuCl_3 in the lattice of TlCuCl_3 (panel(c)) and TlCuCl_3 in the lattice of KCuCl_3 (panel(d)) along the symmetry directions $\Gamma = (0\ 0\ 0)$, $B = (-\pi, 0, 0)$, $D = (-\pi, 0, \pi)$, $Z = (0, 0, \pi)$, Γ , $Y = (0, \pi, 0)$, $A = (-\pi, \pi, 0)$, $E = (-\pi, \pi, \pi)$.
3. Tl(solid) and K(dotted) contributions to the density of states of TlCuCl_3 and KCuCl_3 respectively.

TABLE CAPTIONS

I. Hopping integrals obtained from our ab initio analysis for TlCuCl_3 , KCuCl_3 and the two model systems considered in the text and magnetic interactions from ref. [7] and ref. [8] for TlCuCl_3 and KCuCl_3 . The negative sign denotes a ferromagnetic coupling.

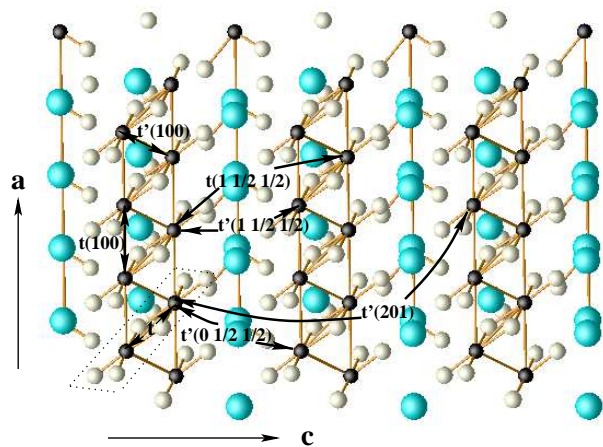


Fig. 1 – .

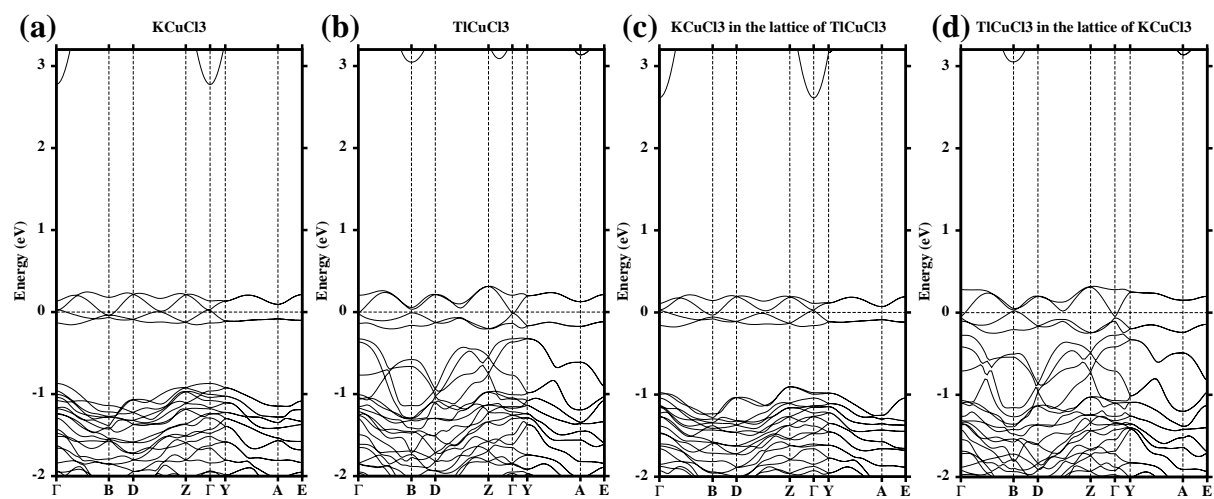


Fig. 2 –

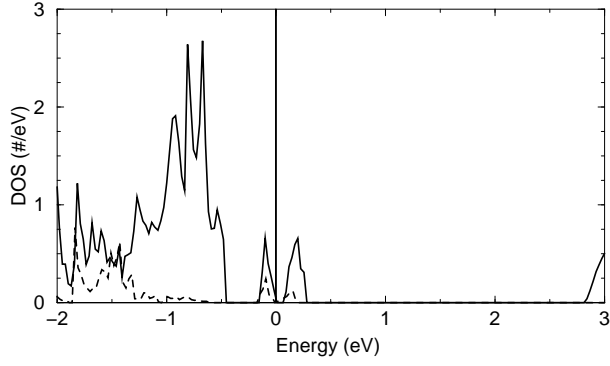


Fig. 3 –

TABLE I –

t's and J's in meV	KCuCl_3	TlCuCl_3	TlCuCl_3 in KCuCl_3 lattice	KCuCl_3 in TlCuCl_3 lattice
t J	116 4.34 ref [8] 4.29 ref [7]	134 5.68 ref [8] 5.42 ref [7]	144	117
t(100) t'(100) $J_{eff}(100) =$ $1/2[2J(100) - J'(100)]$	2.72 9.52 -0.21 ref [8] -0.21 ref [7]	6.81 21.76 -0.46 ref [8] -0.47 ref [7]	4.08 24.49	1.00 5.40
t'(201) $J_{eff}(201) =$ $-1/2J'(201)$	36.73 -0.45 ref [8] -0.34 ref [7]	65.31 -1.53 ref [8] -1.43 ref [7]	72.11	35.37
t(1 1/2 1/2) t(1 -1/2 1/2) t'(1 1/2 1/2) $J_{eff}(1 1/2 1/2) =$ $1/2[J(1 1/2 1/2) - J'(1 1/2 1/2)]$	40.82 4.08 5.19 0.28 ref [8] 0.37 ref [7]	36.73 32.18 12.24 0.49 ref [8] 0.62 ref [7]	42.17 40.50 10.88	35.40 2.72 8.16
t(0 1/2 1/2) t'(0 1/2 1/2) $J_{eff}(0 1/2 1/2) =$ $1/2[J(0 1/2 1/2) - J'(0 1/2 1/2)]$	5.44 14.97 -0.003 ref [8]	8.16 19.05 -0.06 ref [8]	6.80 16.33	8.01 17.63